PB82-234618

Sampling for High-Molecular-Weight Organic Compounds in Power Plant Stack Gases

Southern Research Inst.
Birmingham, AL

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

May 82

U.S. Department of Commerce
National Technical Information Service
NTIS

PB82-234618

EPA 600/7-82-039
May 1982

SAMPLING FOR HIGH-MOLECULAR-WEIGHT ORGANIC COMPOUNDS IN POWER PLANT STACK GASES

by

Walter R. Dickson
Herbert C. Miller
William J. Barrett
Southern Research Institute
P. O. Box 3307-A
Birmingham, AL 35255

Contract No. 68-02-2272

Project Officer

Roy L. Bennett
Emissions Measurement and Characterization Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/7-82-039	ORD Report	PB82-234618

4. TITLE AND SUBTITLE	5. REPORT DATE
SAMPLING FOR HIGH-MOLECULAR-WEIGHT ORGANIC COMPOUNDS IN POWER PLANT STACK GASES	May 1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Walter R. Dickson, Herbert C. Miller and William J. Barrett	SORI-EAS-80-387
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Southern Research Institute 2000 Ninth Avenue, South Birmingham, Alabama 35205	CABN1D/05-2208 (FY-82)
	11. CONTRACT/GRANT NO.
	Contract 68-02-2272
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	Final
	14. SPONSORING AGENCY CODE
	EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The results of laboratory and field investigations of experimental sampling systems intended to collect high-molecular-weight organic compounds from flue gases in coal-fired power plants are presented. The most promising sampling device was a solid sorbent cartridge inserted directly into the flue gas stream and cooled to a temperature just above the dew point by a forced flow of external ambient air. Although certain sorbent materials were shown to be partially effective for the collection of vapors of polynuclear aromatic hydrocarbons at temperatures of 50 to 60 °C, no completely satisfactory sorbent was found. Ambersorb XE-340, a nonpolar carbonaceous sorbent, was the most satisfactory of several organic and inorganic sorbent materials tried, but its usefulness was limited by the presence of contaminants that could not be removed. The simplicity of the sampling system and the results obtained suggest that continuing efforts should be made to find a better sorbent material.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	50
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendations for use.

ABSTRACT

This report presents the results of laboratory and field investigations of experimental sampling systems intended to collect high-molecular-weight organic compounds from flue gases in coal-fired power plants. The most promising sampling device was a solid sorbent cartridge inserted directly into the flue gas stream and cooled to a temperature just above the dew point by a forced flow of external ambient air. Although certain sorbent materials were shown to be partially effective for the collection of vapors of polynuclear aromatic hydrocarbons at temperatures of 50 to 60 °C, no completely satisfactory sorbent was found. Ambersorb XE-340, a nonpolar carbonaceous sorbent, was the most satisfactory of several organic and inorganic sorbent materials tried, but its usefulness was limited by the presence of contaminants that could not be removed. The simplicity of the sampling system and the results obtained suggest that continuing efforts should be made to find a better sorbent material.

CONTENTS

Abstract..... iii
Figures..... vi
Tables..... vii
Acknowledgments.....viii

1. Introduction..... 1
2. Conclusions and Recommendations..... 4
3. Evaluation of Modified EPA Method 5 Trains..... 7
   - Apparatus and Methods..... 7
   - Tenax-GC Sorbent Beds..... 9
   - Amberlite XAD-2 Sorbent Beds..... 13
   - Reagent Solutions in Combination with XAD-2..... 14
4. Investigations of In-Stack Sampling with Solid Sorbents..... 20
   - Sample Collection at Stack Gas Temperatures..... 20
   - Construction and Evaluation of In-Stack Sorbent-Tube Cooling System..... 32

Preceding page blank

FIGURES

Number		Page
1	Typical experimental stack sampling train based on the EPA Method 5 train	8
2	Representative FID chromatogram of a pentane extract of a flue gas sample collected on Tenax-GC	12
3	Total ion current chromatogram of the pentane extract of a flue gas sample collected on XAD-2	15
4	Experimental stack sampling train for in situ classification of effluent components	18
5	Sampling train with the "In-Stack" sorbent tube for collection of organic material	21
6	Simulated-flue-gas generator	23
7	Modified Tracor Model 560 gas chromatograph. Desorption mode	24
8	Desorption of sorbent tube in heated injection port of the gas chromatograph	25
9	Reconstructed gas chromatogram of representative PAHs desorbed from OV-101 Sorbent	28
10	Reconstructed gas chromatogram of components desorbed from an OV-101 sorbent tube used for field sampling	29
11	Gas chromatogram of desorbed material from Gas-Chrom Q Sorbent	31
12	Air-cooled sampling probe	33

FIGURES (Continued)

Number		Page
13	Modified system for thermal desorption and transfer of sorbate to pre-column at atmospheric pressure	35
14	Flame ionization detector chromatograms of flue gas samples adsorbed on Gas-Chrom Q	41

TABLES

Number		Page
1	Laboratory Evaluation of Sampling Train with Tenax-GC Sorbent Beds	10
2.	Compounds Identified in Power Plant Emissions	16
3.	Efficiency of the Proposed Sampling Train with XAD-2 Slurries	17
4.	Sorption and Desorption of PAH on Ambersorb XE-340	39

ACKNOWLEDGMENTS

Ruby H. James, Christina H. Duffey, and Marcia G. Nishioka participated in the laboratory work on this project. Philip D. King and John C. Harmon assisted in the field sampling.

SECTION I

INTRODUCTION

This project was concerned with the development and evaluation of methods for the identification and measurement of organic materials derived from energy-related sources. The kinds of energy sources of interest were those utilizing the fossil fuels, coal and petroleum, and in particular, coal-burning electric power plants. Emphasis was to be placed on high molecular weight compounds, defined as organic substances that condense at ambient temperatures. It was desired to develop methods that would permit the separation and isolation of specific classes of organic compounds so that those classes or fractions having a significant degree of toxicity could be identified by appropriate bioassay tests.

It was recognized that for the purposes of this project the characterization of organic emissions involved the following general problem areas:

- Collection of samples.
- Separation techniques for classifying types of organic emissions.
- Identification of classes and individual compounds.
- Assessment of potential health effects.

In each of these general areas difficulties of a specific nature were expected to be encountered. Examples of such specific types of problems include the following:

- The presence in stack emissions of relatively high concentrations (relative to organic concentrations) of inorganic species such as the sulfur and nitrogen oxides, inorganic particulate materials (for example, fly ash), and water vapor.
- The nature of the distribution of organic materials between gas and particulate phases.
- The expected low concentrations of organic compounds of interest.

- The necessity of collecting samples of sufficient size to permit chemical and biological characterization.
- The probable complexity of the organic phases in stack gases and the resulting difficulties of separation and identification.
- The problems associated with the relatively high temperature of stack gases at accessible sampling points.

The initial approach taken to solve the problems of sample collection was based on modification of the sampling train described by Diehl, which had previously been used with some success in sampling flue gas for polynuclear aromatic hydrocarbons (PAH).[1] Components of the EPA Method 5 sampling train were used to assemble the experimental sampling systems.[2] The principal modification proposed was the incorporation of a bed of a porous polymer solid sorbent into one of these trains to collect organic vapors. At the time at which this project was initiated little work involving the use of solid sorbents—such as Tenax-GC, the Porapaks, or the Chromosorbs—in sampling flue gases for organic compounds had been reported. Other applications of these materials, however, suggested that they should be useful.

Efforts during the first half of this project were, therefore, directed toward the incorporation of solid sorbent beds into several different configurations of the EPA Method 5 train. Concurrent and more intensive research in other laboratories that led to the development of the EPA Source Assessment Sampling System (SASS) caused us to redirect our efforts about midway in this project.[3,4] Instead of focusing on an external sampling system based on the EPA Method 5 train, we then began an investigation of the use of solid sorbent probes in-stack, either at flue gas temperature or with an air-cooled sorbent tube. All of the sampling investigations were designed to avoid condensation of water vapor on the sorbent, that is, to sample for organic materials with a dry sorbent. This approach differs from that used in the SASS train, in which water vapor condenses in the module containing the sorbent resin. To avoid condensation it is necessary to maintain the sorbent at a temperature above the

---

1. Diehl, E. K., F. duBrevil, and R. A. Glenn, J. for Engr. Power, 89, 276 (1967).
2. Federal Register, Vol. 42, No. 160, Part II, August 18, 1977, pp. 41776-41782.
3. Jones, P. W., R. D. Giammar, P. E. Strup, and T. B. Stanford, "Efficient Collection of Polycyclic Organic Compounds from Combustion Effluents", Environ. Sci. Technol. 10, 806 (1976).
4. Blake, D. E., "Source Assessment Sampling System: Design and Development", EPA Report 600/7-78-018, February 1978.

dew point of the sample gas, typically about 50 to 60 °C; this requirement imposes a severe constraint on the selection of practically useful sorbents.

Thermal desorption was the primary method used for recovering organic materials from the solid sorbents. This technique has certain advantages over solvent extraction in simplicity and speed, especially when the amount of sorbent is only 10 to 20 mg, as it was in most of this work. Usually, desorbed organic vapors were transported from the sorbent tube directly into the analytical column of a gas chromatograph by the carrier gas stream. Separated components were detected by flame ionization or by mass spectrometry.

This report summarizes the results of the earlier investigations, some of which have been subsequently confirmed by others. The results of the in-stack sampling experiments are described more fully. Although that technique appears to have some promise, additional investigations—particularly in field sampling at a number of different plants—are needed to establish its usefulness and validity.

The gas chromatographic inlet system modified for thermal desorption of polynuclear aromatic hydrocarbons (PAHs) collected on sorbent tubes, which was developed under this project (see Section 4), was described in an article submitted to a scientific journal.[5]

---

5. Fowler, William K., Christina H. Duffey, and Herbert C. Miller, Anal. Chem., 51, 2333 (1979).

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The initial efforts on this project were directed toward the collection of organic materials from flue gas with a sampling system based on the use of porous polymer solid sorbents. The sampling system consisted of a modified EPA Method 5 sampling train operated outside the stack and containing a sorbent bed maintained at a temperature above the dew point. This approach was discontinued when it became apparent that it duplicated in some degree developments occurring in other laboratories. Some of the results obtained are, however, of interest and may be summarized as follows:

- Amberlite XAD-2 (Rohm and Haas, Inc.) was found to be superior to Tenax-GC (Enka N.V.) as a sorbent for organic compounds in flue gases. At about 50 °C, XAD-2 is a more efficient sorbent for high-molecular-weight organic compounds than Tenax-GC. Moreover, Tenax-GC is unsuitable because of the formation of an artifact as a result of reaction with nitric oxide.

- Estimates of the total concentration of organic compounds in flue gas that were measured with a porous polymer sorbent held at 50 to 60 °C were of the order of 0.2 mg/m^3. The concentration of total volatile organics, as measured by gas chromatography with flame ionization detection, was estimated to be about 10 mg/m^3 (as methane). High-molecular-weight organics thus represented about 1 to 2% of the total organics in these particular flue gas samples.

- Gas chromatography/mass spectrometry/computer analyses of one flue gas sample collected on XAD-2 and extracted with pentane in a Soxhlet apparatus revealed the presence of about 30 identified compounds, which included several PAHs, a number of paraffins, and several oxygenated organic compounds.

- Elemental selenium (the red, amorphous allotrope) and boric acid were identified by mass spectrometry in condensed deposits in the sampling trains. Their concentrations in the flue gas were estimated to be on the order of several hundred micrograms per cubic meter. Traces of boron trifluoride were also detected. As far as is known, the

presence of these substances in flue gas sampling systems has not been reported previously.

A second approach to sampling that was investigated was based on the insertion of a solid sorbent sampling probe directly into the flue gas, either with or without provision for cooling the sorbent with a forced flow of ambient air. Although a full evaluation of this approach was not completed, sufficiently favorable results were obtained to justify a recommendation that certain aspects of the investigation be pursued further. These recommendations are listed below following a summary of the principal conclusions and results derived from this phase of the project.

The conclusions and results of primary significance were the following:

- Laboratory evaluation of certain sorbent materials under simulated flue gas conditions gave favorable indications of probable suitability for field sampling applications. In some instances, however, serious deficiencies were observed when actual field sampling was attempted.

- Amberlite XAD-2 lacks thermal stability at the temperatures of 300 °C or above that are necessary for desorption of PAHs.

- The silicones OV-101 and SP 2250, which are widely used as high temperature GC column packing materials, react with flue gas constituents to produce relatively large amounts of volatile siloxanes. These siloxanes prevent the gas chromatographic identification of organic compounds that might be present in the sample.

- Carbopack B HT 100, a carbonaceous sorbent containing Dexsil 300 as a liquid phase, absorbs large amounts of sulfur dioxide from flue gas, which interferes seriously with the measurement of any desorbed organic compounds.

- Carbopack B HT, which is similar to Carbopack B HT 100 except that it does not have the Dexsil 300 coating, is an effective sorbent for PAHs at 50 to 60 °C; however, these compounds cannot be desorbed thermally.

- Ambersorb XE-347, another carbonaceous sorbent, also retains PAHs so strongly that they cannot be desorbed thermally.

- Ambersorb XE-340, which is less extensively carbonized than XE-347, is an effective sorbent for PAHs and, under carefully controlled conditions, releases PAHs nearly

quantitatively on thermal desorption. This material, however, contains background PAH impurities that can interfere if the conditions for desorption are not rigidly controlled.

- Gas-Chrom Q is an inorganic material that has a relatively low breakthrough volume for PAHs and is therefore not highly retentive at 50 to 60 °C. Nevertheless, it was a satisfactory sorbent under a limited range of laboratory conditions. Field tests, however, did not yield any evidence of the presence of PAHs in the samples that were analyzed.

- In an effort to find a suitable means of removing water vapor from flue gas without removing PAHs—thereby lowering the dew point and permitting sampling with solid sorbents at a lower temperature—PermaPure drying tubes were evaluated. These devices performed the desired function effectively, but under sampling conditions they also released excessive quantities of what were apparently thermal decomposition products of the NAFION membrane that serves to separate water vapor from other gases.

The following general recommendations are made as a result of the work accomplished under this project:

- A wider range of sorbent materials should be evaluated for in-stack flue gas sampling. Although no fully satisfactory material was found in this work, certain ones came fairly close to meeting the requirements for the collection of PAHs. There is an expanding need for sampling methods, as well as for analytical and bioassay methods, to assess the emissions of health-related organic substances from fossil-fuel combustion sources.

- The air-cooled sampling probe showed considerable promise as a simple device to collect samples of organic compounds. Combined with a sorbent that could be used effectively at 50 to 60 °C, this system could have extensive use.

- An improved sampling system should be evaluated at a number of power plants where conditions could be expected to vary with coal composition, boiler design, and control device performance. All of the field work on this project was conducted at the same 700-MW power-generating unit, where, it is believed, combustion conditions were such that organic effluents were minimal.

SECTION 3

EVALUATION OF MODIFIED EPA METHOD 5 TRAINS

Several variations of components and arrangements of components in the sampling train were evaluated. The general objective was to obtain the maximum efficiency of collection and recovery of organic vapors for subsequent identification and measurement. The experimental approach generally consisted of laboratory evaluation of a sampling system with known amounts of representative organic compounds, followed by field operation of the system at a large (700-MW) coal-burning power plant unit. Samples collected in field tests were subjected to limited analyses, aimed principally at system evaluation rather than extensive characterization of the materials collected.

APPARATUS AND METHODS

Certain basic components of the EPA Method 5 train were not changed in these experiments. They included the probe, the heated cyclone and filter, the ice-water cooled impingers, and the terminal components. The number and locations of the sorbent beds, however, were varied, and two different sorbent materials—Tenax-GC (Enka, N.V.) and Amberlite XAD-2 (Rohm and Haas)—were evaluated. The sorbent beds containing 10 or 20 g of polymer were maintained at either ambient temperature or at a temperature above the dew point, depending on their location in the system.

Figure 1 is a schematic drawing showing the basic components that were included in the sampling train. In some experimental sampling runs two heated sorbent beds were placed between the cyclone oven and the impinger bath, and in others only one. In one trial system, the sorbent bed was located after the impinger bath. In certain runs, separate sorbent beds were used, one containing Tenax-GC and the other XAD-2. Thus, various combinations were tried. A typical sampling train contained the following components: probe; heated sampling line; standard Method 5 cyclone and glass-fiber filter in an oven at 200 °C; a 2.5-m length of coiled, 4-mm i.d. glass tubing (heat exchanger); a bed of 10 g of sorbent supported in a coarse fritted-glass filtering tube at ambient temperature or at a temperature just above the dew point (45-55 °C); three empty 500-mL impingers in an ice bath; another sorbent bed (in some instances); a Drierite tower; a dry test meter; and a pump. The exposed connecting lines were

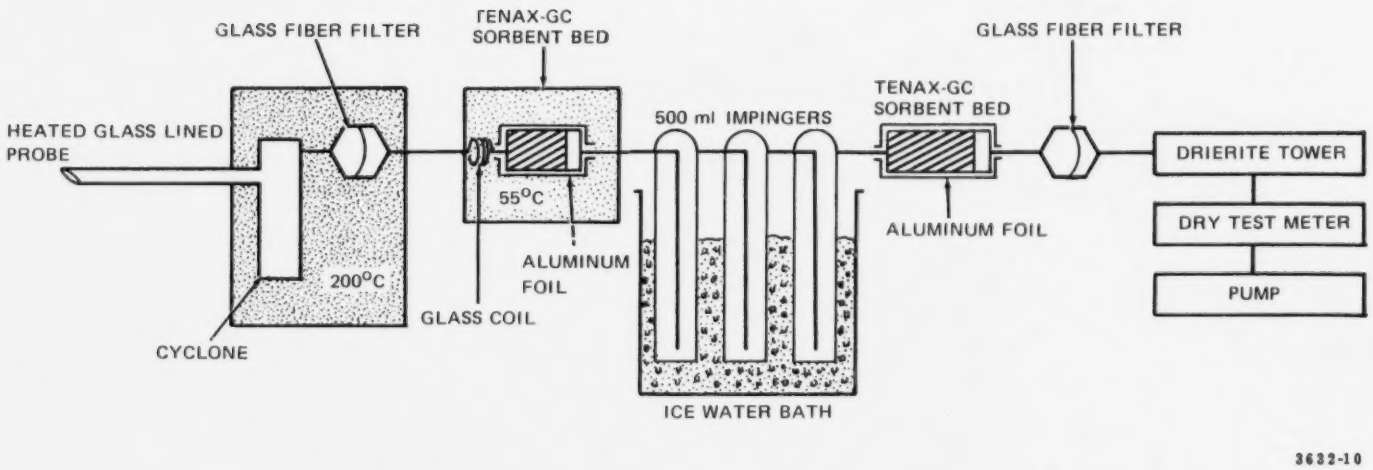

Figure 1. Typical experimental stack sampling train based on the EPA Method 5 train.

wrapped with heating tape and the filter funnels that contained the sorbent were wrapped with aluminum foil. Flow rates were usually 20 to 30 L/min.

Sorbent samples were extracted in a Soxhlet apparatus with cyclohexane, pentane, or ethanol. Because of evidence of some oxidation of cyclohexane during long extraction periods, pentane was considered to be the better of these two nonpolar solvents. Ethanol was used in some instances following exhaustive extraction with cyclohexane or pentane. In an experimental comparison of Soxhlet extraction with ultrasonic extraction, the former was found to be superior for removing naphthalene and anthracene from Tenax-GC; 85 to 90% recoveries were obtained in a 24-h Soxhlet extraction while a total of 50 to 60% was obtained in three successive ultrasonic extractions of 40, 20, and 20 min. A similar conclusion was reached on comparing the two methods for extracting field samples. Extracts were concentrated by evaporation in a Kuderna-Danish concentrator. Components of the sampling train other than the sorbent itself were washed with cyclohexane to remove deposited organic materials.

Analyses of extracted materials were conducted by ultraviolet absorption spectrophotometry, gas chromatography with flame ionization detection, and by gas chromatography/mass spectrometry/data system. UV absorption was used to obtain an approximate measure of total amounts of organic compounds, gas chromatography to indicate the degree of complexity, and gas chromatography/mass spectrometry to identify specific compounds.

TENAX-GC SORBENT BEDS

Laboratory Evaluation

Experiments were conducted to determine the efficiency of collection and recovery of four selected compounds—naphthalene, anthracene, phenol, and benzaldehyde. The sampling train contained two Tenax-GC sorbent beds, one between the cyclone-filter oven and the impinger bath, and another following the impinger bath. Each of the test compounds was introduced individually by depositing 100 µL of a solution containing 300 µg of the compound on a small strip of filter paper at the inlet end of the sampling probe. The solvent and the test compound were evaporated by drawing hot air (ca. 150 °C) over the paper strip and into the probe. Air was drawn through the system at about 20 L/min for 30 to 60 min. The two sorbent beds were extracted with cyclohexane in a Soxhlet apparatus, and all other components of the train were rinsed with cyclohexane. The solutions were analyzed by ultraviolet absorption spectrophotometry.

The results of these experiments are shown in Table 1. Data are given for experiments conducted with the first sorbent

bed at ambient temperature and also at 45 to 49 °C, a temperature range estimated to be above the dew point of the stack gas. (The second sorbent bed was always at ambient temperature.) No measurable amounts of any of the four compounds were found in any of the rinse solutions or in the filter extracts. The compounds occurred only in the extract of the first sorbent bed; none was detected in the second bed in any experiment. As shown in Table 1, recoveries were not complete, except for naphthalene, presumably because of losses during the sampling period or because of incomplete extraction from the sorbent. The relatively poor recovery of phenol was not unexpected, since that compound probably is the most difficult of the four to extract and measure.

TABLE 1. LABORATORY EVALUATION OF SAMPLING TRAIN WITH TENAX-GC SORBENT BEDS

Compound	Percent recovery of compound	
	25 °C	45-49 °C
Naphthalene	100	100
Anthracene	84	77
Phenol	49	43
Benzaldehyde	76	64

Field Evaluation

Two sampling trains were used on several occasions to collect a number of samples at the 700-MW coal-fired power plant. (All field work on this project was done at the same location.) One train contained a single Tenax-GC sorbent bed following the ice-cooled impinger bath (condensate trap). The second train had two sorbent beds—one maintained at 55 °C, or at 45 °C, ahead of the impinger bath and one at ambient temperature following the impinger bath. Several samples were taken at the outlet of the electrostatic precipitator where the gas temperature was approximately 150 °C. Gas sample volumes were in the range of 2 to 3 m^3 and sampling flow rates were 20 to 36 L/min.

Solvent (cyclohexane) rinses of the various components of the trains, the aqueous condensates, and Soxhlet extracts of the sorbent beds were analyzed by ultraviolet spectrophotometry. The results indicated that no appreciable percentage of the total UV-absorbing organic material was collected in the probe, sampling lines, cyclone, and filter. The aqueous condensate tended to concentrate the more polar water-soluble compounds in both types of trains. Less soluble compounds were collected as a separate phase in the impinger; solutions of this material had UV spectra similar to those of extracts of the sorbent beds. In the train

having two Tenax-GC sorbent beds (separated by the ice-cooled impingers) the amount of UV-absorbing material collected by the second bed was 50 to 90% of the amount collected on the first bed. Generally, the most significant absorption bands occurred at 230, 330, and 380 nm.

Pentane extracts of the Tenax-GC beds from the two sorbent-bed train were analyzed by gas chromatography with flame ionization detection. Figure 2 is a representative chromatogram of a typical pentane extract. Most samples had numerous small peaks, and some had as many as eight peaks that could be described as major peaks. By calibrating the FID response with perylene standards, it was estimated that the total concentration of volatile organic compounds in one stack gas sample (985 liters) was about 0.4 mg/m^3, and in another (1225 liters) about 1.0 mg/m^3. It was estimated that approximately 75% of the measurable organic material was collected on the first sorbent bed, in general agreement with the results obtained by ultraviolet absorption measurements.

After the first few Soxhlet extraction cycles, the pentane extracts showed a strong yellow coloration that faded and slowly disappeared as the extraction continued for 24 h. Accordingly, some samples were extracted for 2 h after which the solvent was removed and replaced with fresh solvent; the extraction was then continued for 24 h. About 90% of some of the major constituents was removed in the first 2 h; other, minor, constituents appeared only in the 24-h extract. Subsequent 24-h extractions with ethanol yielded no additional constituents.

On storage of concentrated (Kuderna-Danish) pentane extracts under refrigeration, it was observed that a yellow-orange crystalline material separated from the solution. This material was identified as 2,6-diphenyl-1,4-benzoquinone, an apparent degradation product of Tenax-GC, which is a polymer of 2,6-diphenyl-p-phenylene oxide. The presence of this compound seemed to explain the yellow color of the Soxhlet extracts. Further, it was determined that the quinone represented most of the total organic material that had been estimated to occur in the flue gas. The large GC peak at 18 min in Figure 2 was identified by GC/MS as 2,6-diphenyl-1,4-benzoquinone. Subsequent reports of the occurrence of the quinone suggested that it resulted from the reaction of Tenax-GC with the nitric oxide in the flue gas.[6]

Because of its apparent low efficiency for collecting at least some types of organic compounds, and especially because of the formation of relatively large proportions of the quinone artifact, it was concluded that Tenax-GC was not a satisfactory sorbent material for flue gas sampling.

---

6. Neher, M. B., and P. W. Jones, Anal. Chem., 49, 512 (1977).

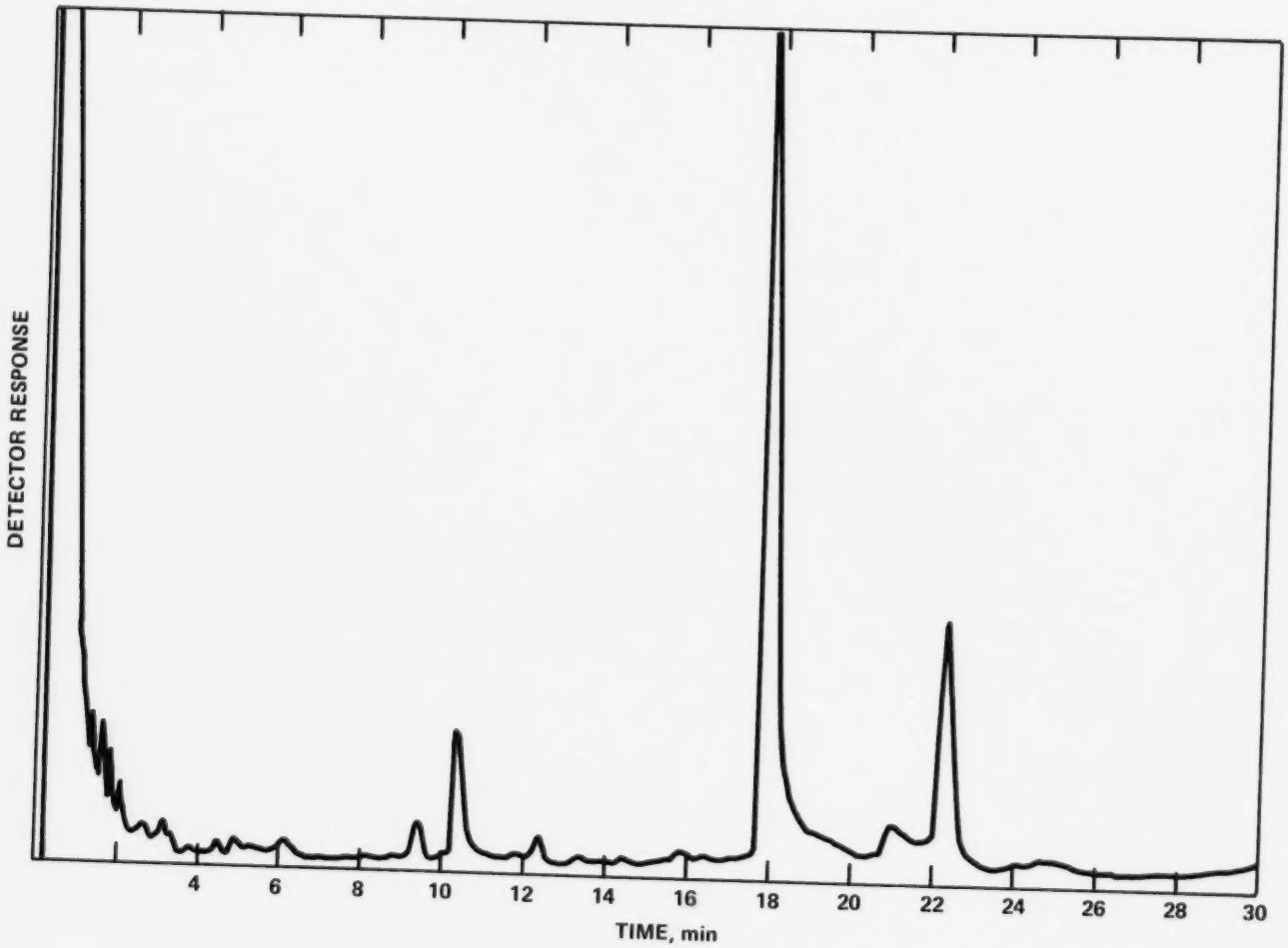

Figure 2. Representative FID chromatogram of a pentane extract of a flue gas sample collected on Tenax-GC.

An observation of incidental interest was the deposition of elemental selenium in the sampling trains. A red deposit in the glass coil between the glass fiber filter and the sorbent bed was identified by mass spectrometry as the red amorphous allotrope of selenium. From its weight and the volume of gas sampled, its concentration in the gas phase was estimated to be about 1 mg/m^3.

AMBERLITE XAD-2 SORBENT BEDS

Laboratory Evaluation

The second sorbent material, Amberlite XAD-2, was cleaned by sequential extraction with water, methanol, diethyl ether, and pentane to remove low molecular weight impurities. The efficiency of collection and recovery of anthracene was determined in the laboratory with the sampling system that was to be used in the field. A glass cooling coil and two 20-g XAD-2 sorbent beds in series were maintained at 45° while a solution containing 150 µg of anthracene was deposited on a strip of filter paper at the inlet. Air at 150 °C was drawn into the inlet to evaporate the anthracene and carry it into the sorbent beds. After 4 h the sorbent beds were extracted with pentane in a Soxhlet apparatus and the extract was analyzed by ultraviolet absorption. After 2 h of extraction approximately 60% of the anthracene was recovered; another 8 h yielded a total of 70% recovery. No anthracene was found in the second of the two XAD-2 sorbent beds.

Field Evaluation

The sampling system consisted of the usual probe, cyclone, filter, empty impingers, and terminal components, but had two 20-g XAD-2 sorbent beds, both at 45 °C, immediately following the cyclone-filter oven. Several 4-h sampling runs were made at the 700 MW-power plant unit.

Ultraviolet absorption spectra of the concentrated pentane extracts indicated that about 70% of the total UV-absorbing organic material was collected in the first sorbent bed. Essentially the same value was estimated from gas chromatographic data obtained with a flame ionization detector. By comparing the total GC/FID responses of the sample components with that of anthracene standards, it was estimated that the total concentration of volatile organic compounds in the flue gas was about 0.2 mg/m^3. This value was in reasonable agreement with total organic concentration determined similarly with Tenax-GC as the sorbent, when an allowance is made for the presence of the quinone artifact formed with Tenax-GC.

A concentrated pentane extract of one of the XAD-2 sorbent beds was analyzed by gas chromatography/mass spectrometry. The

total ion current chromatogram is shown in Figure 3 and the identities of the specific compounds found are given in Table 2. The compounds listed in Table 2 include eight aromatic hydrocarbons, ten paraffins, five phthalate esters, six other oxygenated organic compounds, one sulfur heterocycle, and one chlorine-containing compound. No nitrogen compounds were identified in this sample. The variety of functionalities suggests that the XAD-2 resin did not preferentially collect specific classes of compounds. Several phthalate esters were identified. The source of these ubiquitous compounds could not be definitely established, but they did not occur in the solvent or unexposed resin, or in components of the sampling train other than the sorbent bed itself. Therefore, the possibility that they were present in the flue gas could not be excluded.

The red amorphous allotrope of selenium was also found in the glass tubing and glass wool plugs just preceding the first sorbent bed, where the gas begins to cool from 150 to 45 °C. Additionally, a fine white crystalline material deposited between the second sorbent bed and the impinger was identified by mass spectrometry as boric acid. Traces of boron trifluoride were also detected in this deposit. The concentrations of both selenium and boric acid were estimated to be in the range of hundreds of micrograms per cubic meter.

It was concluded as a result of these experiments that XAD-2 was a better sorbent material than Tenax-GC for the collection of organic vapors at temperatures just above the dew point of water in stack gas—that is, 45 to 55 °C. However, progress made elsewhere toward the development of the EPA's SASS train made it appear unprofitable to pursue this approach further. Therefore a brief investigation of another sampling system was undertaken, as described in the following section. Later, an approach based on in-stack sampling was investigated.

REAGENT SOLUTIONS IN COMBINATION WITH XAD-2

One criterion for the kind of sampling system under consideration was that, insofar as possible, it should effect some degree of separation of organic compounds by classes during the sampling process. In the sampling systems described previously condensation of water in the sorbent bed was prevented by maintaining the temperature of the bed just above the dew point; condensation occurred later in the cooled impingers. The concept now to be described involved the use of acidic or basic solutions in contact with XAD-2 sorbent in impingers. Since porous polymer resins—particularly XAD-2—had been used extensively for concentrating traces of organic materials from water, there appeared to be no compelling reason for avoiding condensation

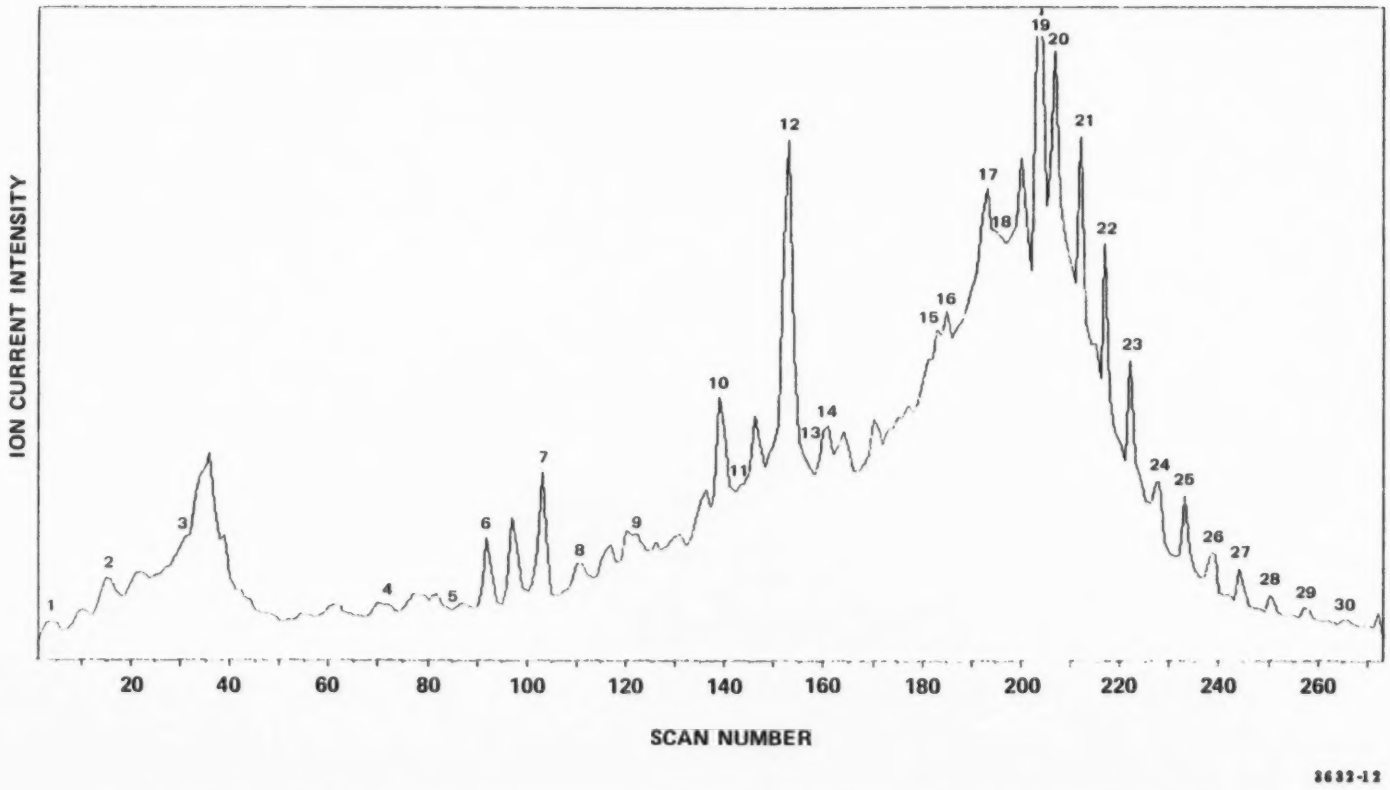

Figure 3. Total ion current chromatogram of the pentane extract of a flue gas sample collected on XAD-2. Peak numbers correspond to compound identification given in Table 2.

TABLE 2. COMPOUNDS IDENTIFIED IN POWER PLANT EMISSIONS

Peak No.*	Most abundant mass	Identity	Empirical formula	Molecular weight
1	133	p-ethyl acetophenone	$C_{10}H_{12}O$	148
2	135	2-t-butyl phenol	$C_{10}H_{14}O$	150
3	105	benzoic acid	$C_7H_6O_2$	122
4	125	2-ethyl-5-isoamylthiophene	$C_{11}H_{18}S$	182
5	166	fluorene	$C_{13}H_{10}$	166
6	149	diethylphthalate	$C_{12}H_{14}O_4$	222
7	105	benzil	$C_{14}H_{10}O_2$	210
8	173	dichlorobenzoic acid	$C_7H_4OCl_2$	174
9	178	diphenyl acetylene or anthracene or phenanthrene	$C_{14}H_{10}$	178
10	149	diisobutyl phthalate	$C_{16}H_{22}O_4$	278
11	192	methylphenanthrene	$C_{15}H_{12}$	192
12	149	di-n-butyl phthalate	$C_{16}H_{22}O_4$	278
13	278	dibenzanthracene	$C_{12}H_{14}$	278
14	202	diphenyl diacetylene or fluoranthene or pyrene	$C_{16}H_{10}$	202
15	219	1-methyl-7-isopropyl phenanthrene or 3,4,5,6-tetramethyl phenanthrene	$C_{18}H_{18}$	234
16	252	benzopyrene or perylene or benzofluoranthene	$C_{20}H_{12}$	252
17	239	methyl dihydroabietate	$C_{21}H_{30}O_2$	314
18	226	benzo[ghi]fluoranthene	$C_{18}H_{10}$	226
19	149	dicyclohexyl phthalate	$C_{20}H_{26}O_4$	330
20	149	diisooctyl phthalate	$C_{24}H_{38}O_4$	390
21-30		a series of high molecular weight hydrocarbons (paraffins)	C_nH_{2n+2}	

*See Figure 3.

of water in the sorbent bed.[7] A stack sampling train incorporating this concept is shown schematically in Figure 4. Components of this train were assembled and evaluated in the laboratory in a simulated stack sampling situation.

A simulant mixture containing about 0.5 mg each of phenol, anthracene, benzoic acid, and docosane was vaporized at 140 °C and introduced into the stack sampling train over a period of 3 h. During this time the train sampled laboratory air at a rate of about 30 L/min.

The distribution of the organic compounds was determined by GC analyses of extracts of the various slurries and sorbent beds. The recovery data are given in Table 3. These data indicate that only a slight degree of in situ separation of the four compounds occurred. The neutral components, anthracene and docosane, were distributed throughout the system, although more than half of each compound was found in the first impinger, which was acidic. The weaker of the two acids, phenol, was found in increasing amounts in the three impingers, with about half retained in the neutral solution in the third impinger, and none in the dry XAD-2 sorbent bed. The benzoic acid was not recovered at all; presumably, it was lost in the parts of the sampling train that preceded the impingers.

TABLE 3. EFFICIENCY OF THE PROPOSED SAMPLING TRAIN WITH XAD-2 SLURRIES

Compound	Recovery, %					Total recovery, %
	Slurry*			Sorbent bed		
	Acid	Base	Neutral	1	2	
Phenol	16	33	51	0	0	100
Anthracene	68	7	11	7	6	99
Docosane	67	10	7	18	14	116
Benzoic acid†	-	-	-	-	-	-

* Recoveries were corrected for extraction efficiencies in sample preparation.

† This component was not recovered (see text).

7. Junk, G. A., J. J. Richard, M. D. Grieser, D. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz, and G. V. Calder, J. Chromatog., 99, 745, 1974.

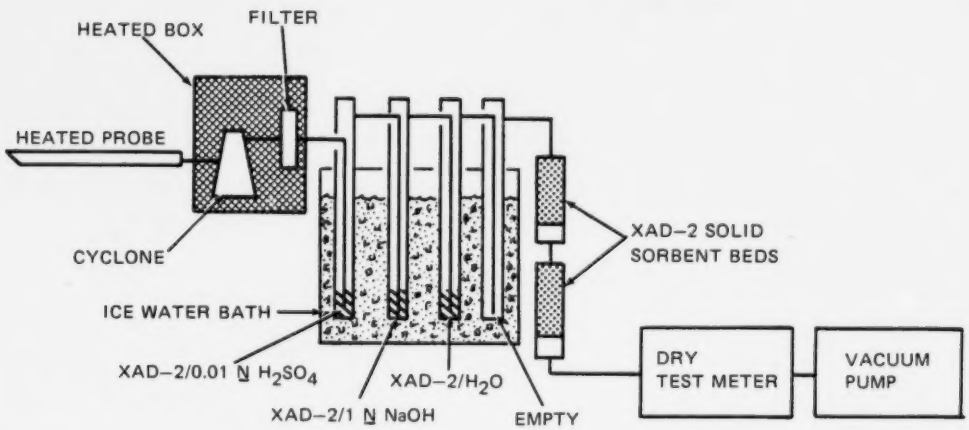

Figure 4. Experimental stack sampling train for in situ classification of effluent components.

The use of reagent solutions was considered to have only marginal promise as the basis for a sampling system, and no further work was done on this subject.

SECTION 4

INVESTIGATIONS OF IN-STACK SAMPLING WITH SOLID SORBENTS

Although a moderate degree of success was obtained with XAD-2 for direct flue gas sampling when the gas was cooled externally (outside the stack) to a temperature just above the dew point, a decision was made to investigate the possibility of sampling with a solid sorbent tube introduced directly into the stack. Such a sampling technique would require that the sorbent collect organic vapors at a temperature in the neighborhood of 150 to 160 °C, or that a means be devised to cool the sorbent bed while collecting a sample. Both of these approaches were investigated.

An advantage of in-stack sampling for organic compounds is simplicity of equipment. Only a probe and a pump are required; or, if cooling were necessary, two pumps might be needed. Practical requirements are that the sorbent material should efficiently retain high-molecular-weight organic compounds at a stack-gas temperature of about 150 °C; that adsorbed compounds remain stable in the presence of other gases such as the nitrogen and sulfur oxides; and that they be capable of being desorbed without chemical change. The approach to chemical analysis was expected to be based on thermal desorption into a gas chromatographic analytical column, with detection with a flame ionization detector or by mass spectrometry.

SAMPLE COLLECTION AT STACK GAS TEMPERATURES

Apparatus and Procedures

The sampling probe is illustrated in Figure 5. The probe consisted of a 1.5-m by 2-cm stainless steel tube fitted coaxially with stainless steel tubing for connection to the Pyrex glass sorbent tubes (shown in Figure 5). Provision was made in the probe for a slip connection to permit the insertion and withdrawal of sorbent tubes. The sorbent tubes were connected to the stainless steel tubing with stainless steel fittings and Teflon ferrules. Each sorbent tube contained two sections of sorbent material held in place by glass wool plugs. The dimensions of the sorbent tube were chosen to permit its insertion into the inlet port of the modified gas chromatograph, as described later.

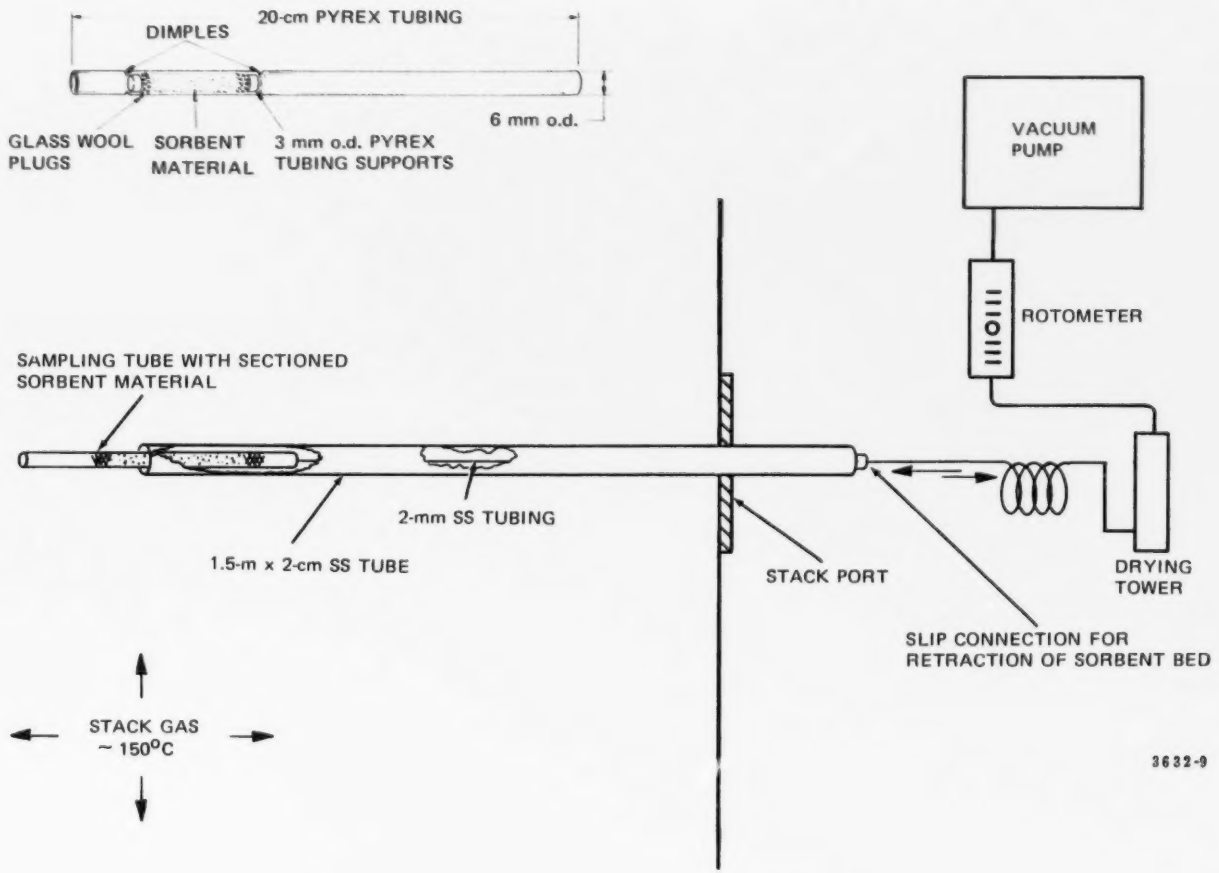

Figure 5. Sampling train with the "In-Stack" sorbent tube for collection of organic material.

For laboratory evaluation of sorbents with known amounts of organic compounds under flue gas conditions, the simulated-flue-gas generator shown in Figure 6 was used. The components of the generator following the furnace were constructed of Pyrex glass and were heated to maintain the temperature above the dew point. The moisture content of the gas stream was controlled by regulation of the syringe-pump water feed rate and the dilution-air flow rate. Organic compounds were introduced as solutions in volatile solvents; the desired vapor concentrations were obtained by appropriate adjustment of the concentration of the solution or the syringe pumping rate. In some instances, solutions of known concentration were injected manually into the heated gas stream with a syringe.

Samples collected on solid sorbents, either in laboratory experiments or in field sampling, were analyzed by gas chromatography with flame ionization detection or by gas chromatography/mass spectrometry. In some experiments—performed to evaluate sorbents with known amounts of specific compounds—a Tracor Model 560 gas chromatograph was used with the sampling arrangement shown in Figure 7. The use of a multiport valve permitted operation in a sampling mode for a period of time, followed by operation in a desorption mode in which collected sample was thermally desorbed and flushed through an analytical column to the flame ionization detector.

In other experiments, in which higher desorption and column temperatures were needed, and in which field-collected samples were to be analyzed, a modified Hewlett-Packard Model 5750 gas chromatograph was used. This equipment is illustrated in Figure 8. The injection port was modified so that it could accept 3-mm o.d. Pyrex sorbent tubes and plumbing was added to provide the necessary gas flow paths. Use of this equipment permitted the thermal desorption of sampling tubes directly into the carrier gas stream. A more detailed description is provided in the journal article prepared by members of the project staff.[5]

Some analyses were performed with a Hewlett-Packard Model 5985 GC/MS system. With this system an external thermal desorption apparatus was necessary; it was connected to the injection port of the GC/MS system with appropriate arrangements for resistance-element heating and for control of gas flow.

Removal of Water Vapor from Sample Gas

Removal of some of the water vapor from the flue gas being sampled would lower the dew point and thereby permit solid sorbent sampling at a reduced temperature. Collection efficiency would be expected to be improved while still avoiding the problems that might be caused by the presence of condensed water. An attempt was made to accomplish this objective by the use of PermaPure air dryers (PermaPure Products, Inc.). This apparatus

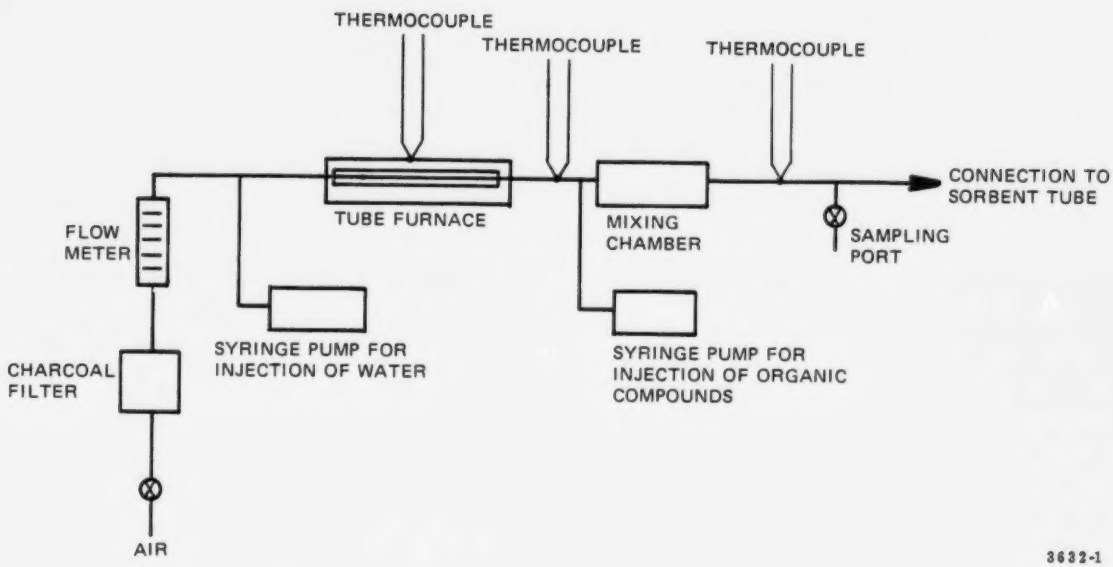

Figure 6. Simulated-flue-gas generator.

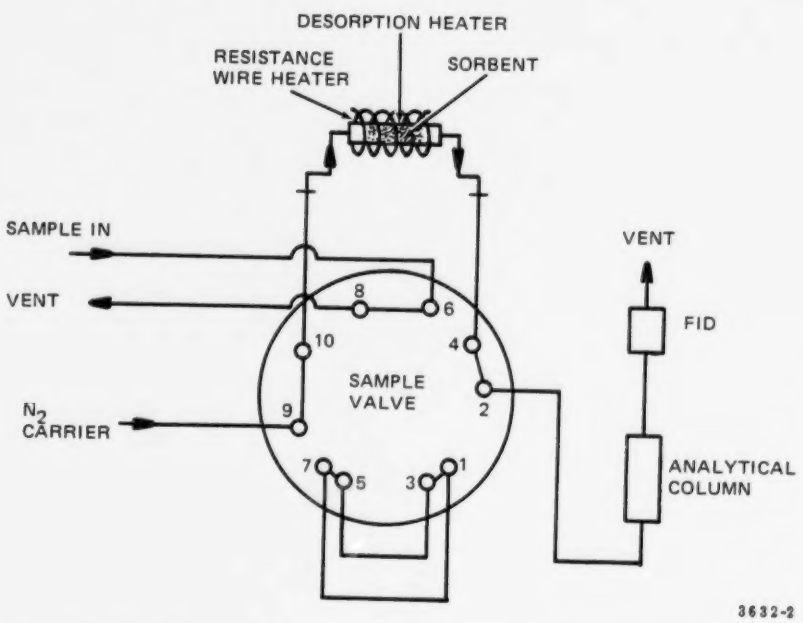

Figure 7. Modified Tracor Model 560 gas chromatograph. Desorption mode.

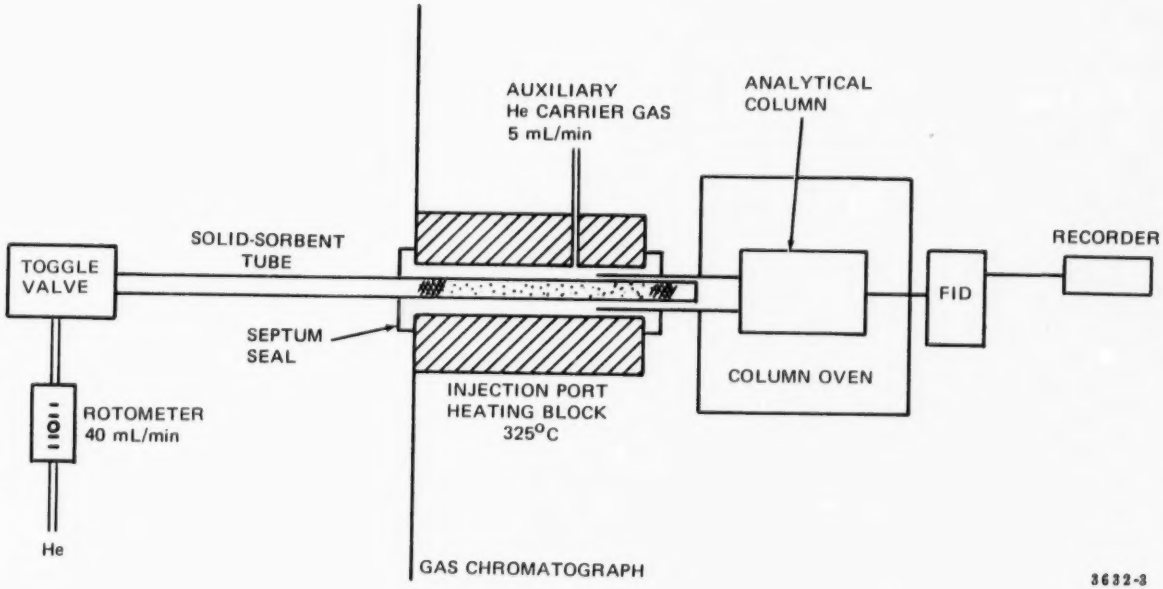

Figure 8. Desorption of sorbent tube in heated injection port of the gas chromatograph. Subsequent transferral of desorbed components onto analytical column with detection by FID and MS.

functions by the permeation of water vapor through a tubular membrane into a dry airstream flowing countercurrently to the sample flow. The membrane is made of NAFION (E. I. du Pont de Nemours, Inc.), a perfluorosulfonic acid polymer. Although some polar organic compounds would be expected to be absorbed by the membrane, hydrocarbons generally are not absorbed.

PermaPure tubes were evaluated at about 130 °C by injecting a mixture of C_7-C_{18} paraffin hydrocarbons into the generator system (Figure 6), passing this sample stream through the PermaPure tubes, collecting the hydrocarbons in a sorbent tube with XAD-2 resin, and thermally desorbing the compounds into the Tracor Model 560 gas chromatograph (Figure 7). Initially, the removal of water vapor was effective, and the recovery of known amounts of the paraffin hydrocarbon mixture was satisfactory. On continued use of the PermaPure tube at the elevated temperature, however, many extraneous, unidentified peaks appeared in the chromatograms. These peaks did not decrease on successive runs, but when the PermaPure tube was replaced by a Teflon tube the artifact peaks disappeared. It was concluded, therefore, that the continued formation of decomposition products from the NAFION membrane precluded use of the PermaPure dryer in a flue gas sampling system.

Evaluation of Sorbent Materials

Practical application of the "in-stack" solid sorbent sampling system required that the sorbent efficiently retain high-molecular-weight organic compounds at stack gas temperatures (ca. 150 °C), that the sorbent and the sorbed compounds remain stable at desorption temperatures of 250 °C or more, and that they be inert to reactive stack gases such as the nitrogen and sulfur oxides. Several types of sorbent materials were evaluated with respect to these principal criteria. These evaluations were conducted by both laboratory bench experiments and by field sampling at the 700-MW power plant unit.

XAD-2--

In the experiments performed to evaluate the PermaPure dryer, it was demonstrated that Amberlite XAD-2 resin (Rohm and Haas, Inc.) effectively collected C_7-C_{18} paraffin hydrocarbons at 130 °C and that these compounds were recovered by thermal desorption with near 100% efficiency. In other similar experiments (without the PermaPure dryer), the compounds n-nonane and n-tetradecane were also collected and recovered with essentially 100% efficiency.

Further experiments were conducted with a known mixture of representative polynuclear aromatic hydrocarbons. Solutions containing known amounts of anthracene, fluoranthene, and chrysene were injected into the generator system (Figure 6) and

evaporated into a heated stream of nitrogen. The vapors were collected in XAD-2 sorbent tubes, desorbed thermally, and measured in the Tracor Model 560 gas chromatograph (Figure 7). With this system it was possible to make injections of the PAH mixture directly on-column for comparison with injections made into the sorbent tube. The conclusion reached from these measurements was that the temperature necessary for effective desorption of the PAHs from XAD-2—250 to 300 °C—exceeded the limit of thermal stability of the resin, and that decomposition products derived from the resin itself precluded its use as a collection medium for PAHs. Therefore, no field sampling was attempted with XAD-2.

OV-101--

The silicone polymer OV-101 is a high-temperature column-packing material used for gas chromatographic separations. Laboratory evaluation of this material was done with sorbent tubes packed with 10% OV-101 on 100/200-mesh Supelcoport (Supelco, Inc.). Mixtures of known amounts of anthracene, fluoranthene, and chrysene were evaporated into a heated nitrogen stream, collected on the sorbent tubes at temperatures of 35, 45, or 70 °C, and desorbed at a temperature of about 300 °C. The analytical system used in this instance was either the Hewlett-Packard Model 5750 gas chromatograph or the Perkin Elmer GC/MS System, in which the sorbent tubes were inserted manually into the heated injection port of the gas chromatograph for thermal desorption. The recoveries of 500-ng amounts of anthracene and fluoranthene were nearly quantitative, and more than 70% of the chrysene, which has the highest boiling point of the three compounds, was recovered. Figure 9 is a representative chromatogram of a sorbed, desorbed, and analyzed mixture.

On the basis of these favorable results in the laboratory, several field samples were collected in OV-101 sorbent tubes inserted directly into the flue gas stream of the 700-MW power-generating unit. Eight sets of samples were collected at a flow rate of about 100 mL/min for periods ranging from 5 to 45 min. On desorption at 310 °C into the GC/MS system, chromatograms similar to that shown in Figure 10 were obtained. The major peaks in the chromatogram in Figure 10 represent several siloxanes. These compounds presumably resulted from reaction of the OV-101 liquid phase with acidic constituents of the flue gas. They did not appear when blank sorbent tubes (not exposed to the flue gas) were similarly processed. Several PAH compounds were detected, as shown in Figure 10, thus demonstrating the ability of OV-101 sorbent to collect these compounds under flue gas sampling conditions. The overwhelming presence of the artifact siloxanes, however, ruled out the practical use of OV-101 for flue gas sampling.

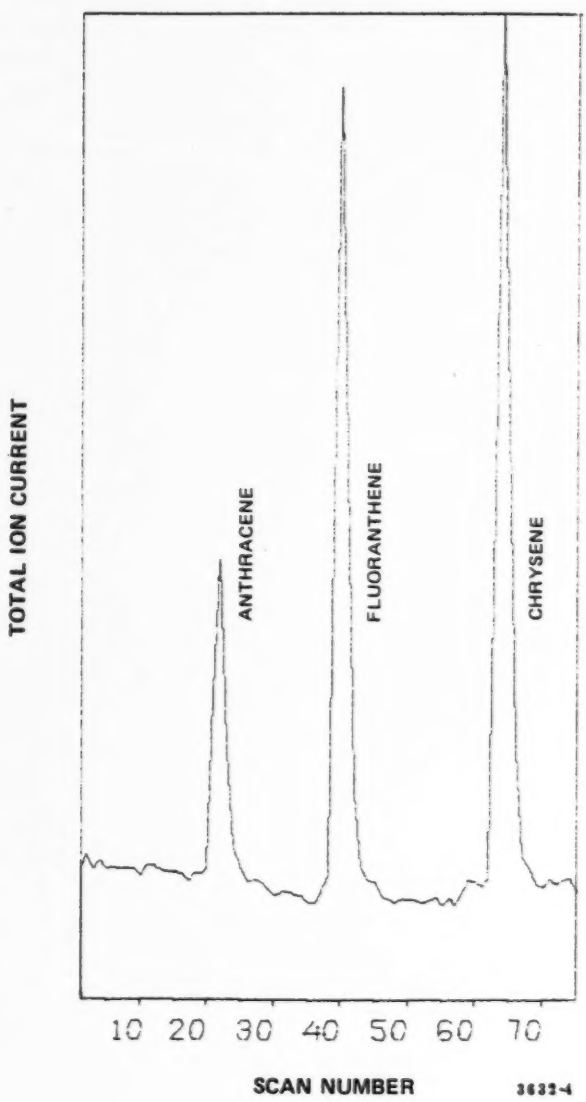

Figure 9. Reconstructed gas chromatogram of representative PAHs desorbed from OV-101 Sorbent (ca. 500 ng each).

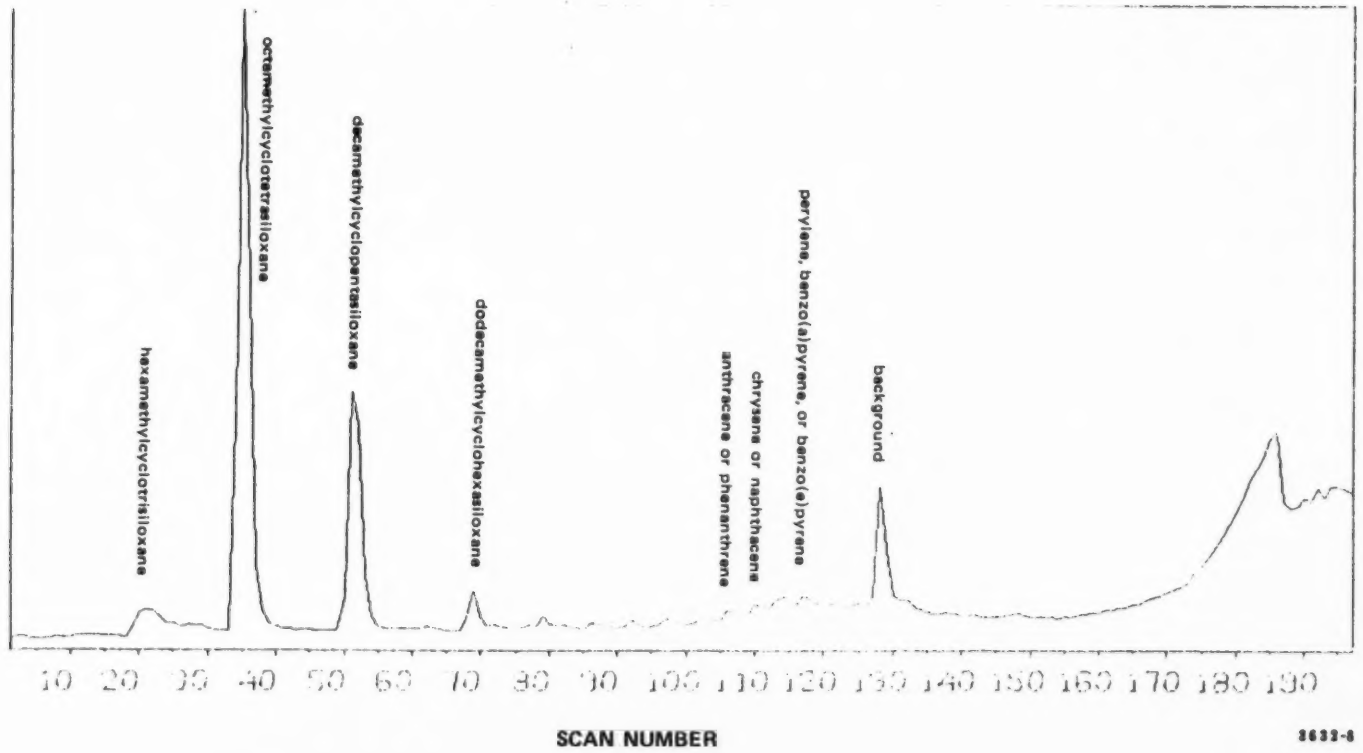

Figure 10. Reconstructed gas chromatogram of components desorbed from an OV-101 sorbent tube used for field sampling.

Gas-Chrom Q--

Gas-Chrom Q (Applied Sciences Laboratories, Inc.), which is prepared from diatomaceous earth and is silanized to eliminate reactive sites, is used as an inert solid support in gas chromatography. Favorable laboratory results were obtained with this material when it was spiked with known amounts of the vapors of anthracene, fluoranthene, and chrysene. Upon desorption at 250 °C into the GC/MS system, recoveries exceeding 90% were obtained for all three compounds. Somewhat lower recoveries were observed, however, when the sampling times were extended to longer periods, in accord with the relatively small breakthrough volumes that might be expected for such a sorbent as a diatomaceous earth.

In field sampling tests at the 700-MW power unit, Gas-Chrom Q tubes were used to collect samples in-stack for 14- and 45-min sampling periods on one occasion, and for 20- and 40-min sampling periods on another occasion. Following desorption at either 210 or 300 °C, the collected samples were analyzed by GC/MS with the Hewlett-Packard Model 5985 system. Several compounds were detected but only one PAH could be identified; it was either biphenyl or acenaphthene. Figure 11 is an example of a chromatogram. Some of the peaks were suspected to represent siloxanes derived from the OV-17 silicone packing that was used in the GC analysis, but were not positively identified. The most significant feature of the results with Gas-Chrom Q was that the peaks in the chromatograms of the 40- and 45-min samples were essentially identical in size to the corresponding peaks in the 15- and 20-min samples. It was thus concluded that Gas-Chrom Q was not an adequately efficient sorbent under flue-gas conditions even though laboratory evaluation had indicated favorable results.

SP-2250--

This methylphenylsilicone (from Supelco, Inc.) was packed in sorbent tubes as a 1% mixture with 100/200-mesh Supelcoport, an inert support. Preliminary laboratory evaluation with a mixture containing anthracene, fluoranthene, chrysene, and dibenzo(a,h)-anthracene resulted in essentially quantitative recovery of each of the first three compounds, and 60% recovery of the least volatile compound, dibenzo(a,h)anthracene (boiling point, 524 °C). Analysis of collected flue-gas samples resulted in the appearance of several siloxane peaks, presumably from reaction of the SP-2250 with flue-gas constituents. Evidence was seen also to suggest that the collection efficiency of SP-2250 was lower when sampling flue gas than when sampling laboratory-generated PAHs. As with OV-101, the reactivity of SP-2250 with flue gas constituents appeared to preclude its use as a sampling medium.

Activated Carbon Sorbents--

Two carbonaceous sorbent materials were evaluated. One of these materials was Ambersorb XE-347 (Rohm and Haas), a polar

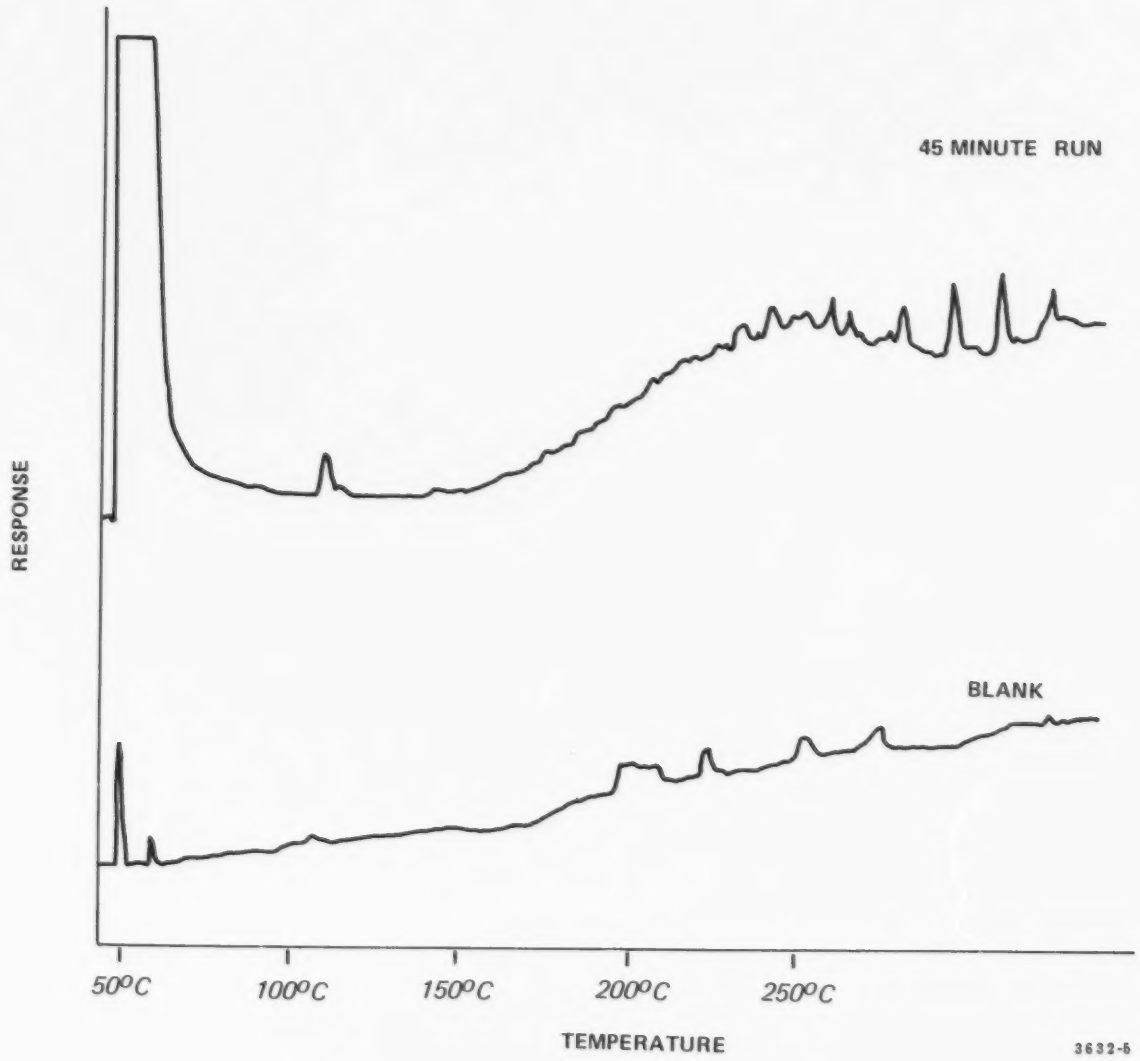

Figure 11. Gas chromatogram of desorbed material from Gas-Chrom Q Sorbent.

macroporous carbon molecular sieve in the form of spherical beads. When tested in laboratory experiments with the selected PAHs (anthracene, fluoranthene, and chrysene), XE-347 was found to retain the compounds completely. Adsorption was, however, irreversible, and recovery by thermal desorption was not possible.

Carbopack B HT 100 (Supelco, Inc.) is a graphitized carbon coated with 0.3% of Dexsil 300 and 0.5% of phosphoric acid. No laboratory data were obtained with Carbopack B-HT 100, but analysis of flue-gas samples showed that it had an excessive affinity for sulfur dioxide, which resulted in an unacceptably high background on thermal desorption into the GC/MS system. Siloxanes also appeared in the chromatograms, presumably resulting from reaction of sulfur dioxide with the OV-17 silicone packing that was used in the GC column. This phenomenon was similar to that observed with Gas-Chrom Q.

The severe deficiencies observed with each of the sorbent materials used to sample flue gases at the prevailing temperature of about 150 °C led to the decision to cool the sorbent tube in place to a temperature just above the dew point, as described in the following section.

CONSTRUCTION AND EVALUATION OF IN-STACK SORBENT-TUBE COOLING SYSTEM

As an alternative to sampling at the typical flue-gas temperature of about 150 °C, an investigation of sampling in-stack with a sorbent tube cooled by a forced flow of ambient air was initiated. The objective was to maintain the temperature of the sorbent bed at a level just above the dew point of the sample gas, that is, at about 50 to 60 °C. Obviously, the efficiency of collection of organic vapors by the sorbent material would be expected to be improved. Although this investigation was not carried fully to completion, the results obtained showed some promise. The following sections describe the apparatus and procedures that were used and give the results of laboratory and field experiments.

Apparatus and Procedures

Sampling Probe--

The air-cooled in-stack sampling probe is illustrated in Figure 12. The sorbent tube was similar to the tube shown earlier in Figure 5. It was enclosed in a Teflon housing through which the cooling air passed and was connected to the sampling pump by a stainless steel tube. This tube was mounted inside a larger stainless steel support tube which also contained thermocouple leads. The thermocouple was located inside the Teflon housing

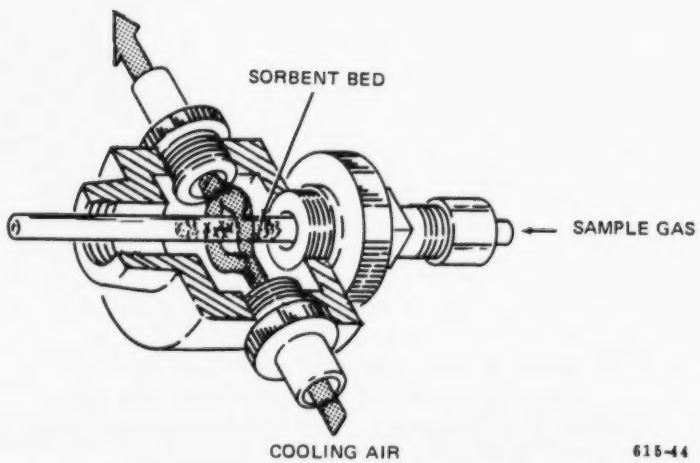

Figure 12. Air-cooled sampling probe.

in contact with the sorbent tube. Cooling air was pumped into the Teflon housing by a Gast pump located outside the flue and equipped with coarse and fine control valves to regulate the air flow rate. The air was pumped through a copper cooling coil to remove the heat generated by the pump itself.

The cooling capacity of this system was determined by placing the sorbent tube end of the probe in an oven at 160 °C and monitoring the gas temperature at the sorbent tube as ambient air was pumped through the housing. The air flow rate was adjusted to give a temperature of 60 °C at the sorbent tube, which would ordinarily be slightly above the dew point.

Modified Desorption System--

The thermal desorption system used in these experiments was somewhat different from that described in Figure 8. Because of evidence that desorption was hindered by the relatively high carrier gas pressure required to obtain an adequate flow rate through the sorbent tube, the system was modified to alleviate this apparent problem. The modified system is shown in Figure 13. The sorbent tube was inserted into the heated injection block or was heated externally in a coil of nichrome wire. A short, jacketed pre-column packed lightly with 3% OV-17 on 80/100-mesh Gas-Chrom Q was connected to the exit end of the injection port of the gas chromatograph inside the oven. A stainless steel tee fitted with a vent valve was placed between the pre-column and the inlet to the analytical column. The jacket around the pre-column permitted cooling of this column with dry ice. With the vent valve open and the pre-column cooled, the sorbent tube was heated to transfer sorbed compounds to the pre-column. In this mode of operation most of the carrier gas was discharged through the vent at near atmospheric pressure. Upon completion of the transfer, the vent valve was closed and the dry ice was removed to allow the pre-column to warm to the oven temperature. The carrier gas then flushed the collected compounds through the analytical column for separation and detection with the flame ionization detector.

This system was tested by instantaneously evaporating known quantities of PAH mixtures (anthracene, chrysene, and perylene) in an empty but heated sorbent tube. The volatilized compounds were collected on the cooled pre-column, as described above, and then re-evaporated and flushed into the analytical column. Another sample of the PAH mixture was then introduced into the system while the pre-column was at the oven temperature and the vent valve was closed. The chromatograms obtained under these two sets of conditions were essentially identical, except for slight differences in the retention times of the individual compounds caused by slightly different dead volumes and slightly different flow rates.

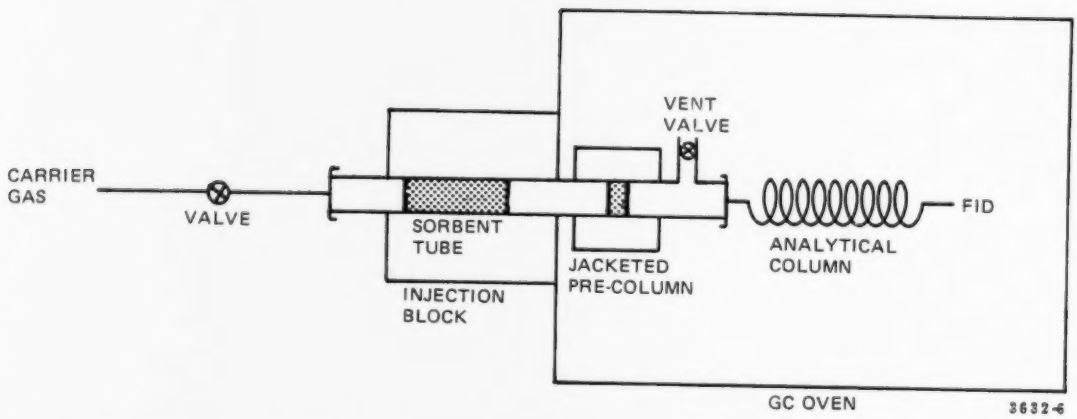

Figure 13. Modified system for thermal desorption and transfer of sorbate to pre-column at atmospheric pressure. In certain instances, the sorbent tube was located outside the injection block and was heated by a coil of nichrome wire wrapped around an external fused silica tube.

High Pressure Liquid Chromatographic Analysis--

Certain field samples collected on Gas-Chrom Q were analyzed by high pressure liquid chromatography (HPLC), a technique that is more sensitive than the GC/MS method. A Hewlett-Packard Model 1084B chromatograph and a Waters Model 420C fluorescence detector were used. The detector had a 360-nm bandpass excitation filter and a 425-nm cutoff emission filter. The analyses were performed with a reverse-phase column with a solvent profile beginning with a 40% acetonitrile-60% water mixture and ending with 100% acetonitrile in 30 min. Sorbent samples were extracted with acetonitrile with the aid of sonic agitation; the extract was concentrated by evaporation and an aliquot was introduced into the HPLC.

The extraction procedure was tested by collecting known amounts (100 ng) of a mixture of the vapors of six PAHs on Ambersorb XE-340 and on Gas-Chrom Q and then extracting and analyzing as described. The six compounds (this mixture was chosen because it happened to be available from another project) were: fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and benzo(ghi)perylene. Recoveries of all of these compounds were 85% or more from either sorbent.

Evaluation of Sorbent Materials

Three sorbent materials were selected for evaluation in the air-cooled sampling probe. They were Gas-Chrom Q, Ambersorb XE-340, and Carbopack B HT. Gas-Chrom Q was shown not to be sufficiently retentive at actual flue gas temperatures; there was, however, sufficient evidence of some recovery of PAHs to justify its evaluation at the lower temperature of 50 to 60 °C. Ambersorb XE-340 is a less polar sorbent than XE-347, presumably as the result of less extensive carbonization in its manufacture from a synthetic polymer. Thus, it was expected that the difficulty encountered in desorbing PAHs from XE-347 would be a lesser problem with XE-340. Carbopack B HT is also a carbonaceous sorbent made from a synthetic polymer, but it does not have the added Dexsil 300 coating that is associated with Carbopack B HT 100; it was therefore expected that Carbopack B HT would not absorb sulfur dioxide to the extent that the coated material does.

In the evaluation of these three sorbents, as described in the following sections, much higher desorption temperatures (400 to 500 °C) were attempted than previously (250 to 300 °C). Generally, the result was that desorption of the less volatile PAHs was more effective at the higher temperatures.

Because of limitations of time, only Gas-Chrom Q was actually used in flue gas sampling. Evaluation of the other two sorbents was limited to laboratory experiments.

Contaminants in Ambersorb XE-340--

During this laboratory study of Ambersorb XE-340 the desorption temperature was taken to levels as high as 500 °C in an effort to remove high-molecular-weight sorbed compounds completely. In the course of these experiments it was discovered that the Ambersorb XE-340 contained PAH impurities that could not be eliminated.

A freshly prepared sorbent tube was conditioned by heating, with carrier gas flowing, to approximately 430 °C for 7 min. The tube was heated outside the GC injection block, as described above (Figure 13), and a gas chromatogram was obtained for the desorbed background contaminant material. The chromatogram showed the presence of a number of organic compounds in substantial amounts. In a second 7-min period of heating at 430 °C, these compounds had essentially disappeared; it was estimated that about 95% of the background contaminants had been removed during the first 7-min heating period. On raising the temperature further to about 475 °C, or upon increasing the time of heating at 430 °C from 7 min to 15 or 20 min, the presence of an even larger quantity of volatile material than was seen originally was shown by the chromatograms.

Additional observations suggested that pressure as well as temperature was a factor involved in the release of background organic materials from XE-340. After two successive 7-min periods of heating at 430 °C, which taken alone would have suggested that 95% of the background contamination had been removed, a sorbent tube was kept at atmospheric pressure in the apparatus shown in Figure 13 for 18 h; on heating this tube again to 430 °C for 7 min, a large quantity of organic material was evolved. Another sorbent tube was treated in the same way except that the pressure was maintained at 350 kPa (50 psi)—instead of atmospheric pressure—for 18 h; on heating this sorbent tube for another 7 min at 430 °C, no more organic material was evolved than during the second 7-min period.

All of these chromatograms were similar except for peak heights. Analyses of the evolved contaminant materials by GC/MS showed that the major components were PAH compounds. The following compounds were identified by mass spectrometry:

anthracene
1-phenylnaphthalene (or 4,5-dihydropyrene)
2-phenylnaphthalene
pyrene (or fluoranthene)
benzo(a)fluorene (or methyl pyrene)
benzo(b)naphtho(1,2-d)thiophene
9,10-benzophenanthrene
chrysene
perylene (or benzofluoranthene)

Efforts were made to remove these PAH contaminants from the XE-340 by Soxhlet extraction for 14 h with benzene and with dichloromethane. After the solvent had been removed by evaporation, the material was packed into sorbent tubes, heated as before for 7 min and then for 15 min. The resulting chromatograms showed no indication that any of the contaminants had been removed by the Soxhlet extractions.

The experimental evidence suggested that these compounds were not simply adsorbed on the surface of the XE-340, but were distributed in the interior of the solid particles and were slowly brought to the surface by diffusion under the influence of increasing temperature or diminishing pressure.

Laboratory Evaluation of XE-340 as a Sorbent for PAHs--

Despite the demonstrated presence of PAHs as contaminants in the XE-340, some favorable results were obtained in experiments in which known amounts of standard PAH compounds were collected, desorbed, and measured. In these experiments the sorbent tubes were subjected to several successive 7-min heating periods and were maintained at the carrier gas pressure of 350 kPa (50 psi). One purpose of these experiments was to demonstrate the performance of the sorption-desorption-analysis system shown in Figure 13. The experiments involved the following four kinds of measurements: (1) injection of a solution containing 200 ng each of anthracene, chrysene, and perylene directly into the GC column (for calibration); (2) deposition and evaporation of the same mixture in an empty heated sorbent tube (to measure the ability of the dry ice trap to retain the PAHs); (3) deposition of the same mixture on the sorbent at room temperature, then heating to 430 °C (to determine whether the compounds could be effectively desorbed at 430 °C); and (4) evaporation of the mixture into a gas stream at 60 °C, passage through the sorbent at 60 °C, then heating to 430 °C (to determine whether the sorbent would efficiently collect the PAHs at 60 °C).

The results are shown in Table 4. They demonstrate that the experimental apparatus (Figure 13) performed satisfactorily and that reasonably satisfactory recoveries of each of the three PAH compounds were obtained under the conditions used. Ambersorb

TABLE 4. SORPTION AND DESORPTION OF PAH ON AMBERSORB XE-340

Process	Average values for recovery					
	Anthracene		Chrysene		Perylene	
	Area	%	Area	%	Area	%
1. Calibration (direct injection on-column)	115	100	43	100	39	100
2. Deposit in empty heated sorbent tube	115	100	44	102	37	95
3. Deposit on sorbent at 25 °C, then heat to 430 °C	71	62	40	93	28	72
4. Sorption of vapor on sorbent at 60 °C, then heat to 430 °C	90	78	33	77	32	82

XE-340 thus has some potential as a sorbent material for PAHs, even though the presence of background contaminants presents a severe difficulty.

Carbopack B HT--

Carbopack B HT is the same carbon as Carbopack B HT 100, which was tested at flue gas temperature, except that it is not treated with Dexsil 300 and phosphoric acid. Carbopack B HT collected a mixture of anthracene, chrysene, and perylene efficiently when used in the laboratory sampling system. None of these compounds could be recovered by thermal desorption, however, even when the sorbent was heated to temperatures in excess of 400 °C. It was concluded that the affinity of Carbopack B HT for PAHs is too strong to permit its use as a sampling medium.

Gas-Chrom Q--

Known amounts of anthracene, chrysene, and perylene were evaporated in the heated inlet of the externally mounted sorbent tube as shown in the sampling system in Figure 13. The vapors were collected on Gas-Chrom Q sorbent tubes at 60 °C. On subsequent desorption at 430 °C, both chrysene and perylene where quantitatively recovered but only about 25% of the anthracene was recovered. In these and similar experiments it was observed that the recovery of the PAHs from Gas-Chrom Q depended on the flow rate and time of sampling. If the total sample of PAHs was collected in 5 min at a flow rate of 40 mL/min, and if the compounds

were desorbed immediately, recovery was quantitative. However, if the flow rate was increased to 1 L/min or if the sampling time was extended to 20 min, significant amounts of the PAHs were lost.

Field Evaluation of Gas-Chrom Q--

Several Gas-Chrom Q sorbent tubes were used to sample flue gas at the outlet of the electrostatic precipitator in the 700-MW unit where the gas temperature at the time was 120 to 130 °C. The sorbent-tube cooling system was used to maintain the temperature of the sorbent tubes at about 60 °C. Gas was sampled at 1.5 L/min for either 14 or 45 min.

Half of these samples were desorbed and analyzed by GC/MS procedures, as described previously. Figure 14 shows chromatograms for a blank and a typical sample. The principal differences in the two chromatograms are in the retention time region of 9 to 12 min. Mass spectral analyses showed that the sample peaks in the 9- to 12-min periods were due to saturated and unsaturated aliphatic hydrocarbons. No PAHs were detected in any of the samples analyzed by GC/MS.

Other samples were extracted with acetonitrile and analyzed by HPLC with a fluorescence detector. Although HPLC is considerably more sensitive to PAHs than GC/MS, and does not detect aliphatic hydrocarbons, there was no evidence of the presence of any PAHs in these samples. It was estimated that, if sample collection and recovery were 100% efficient, a concentration of an individual PAH in the flue gas of at least as little as 1 $\mu g/m^3$ would have been detected.

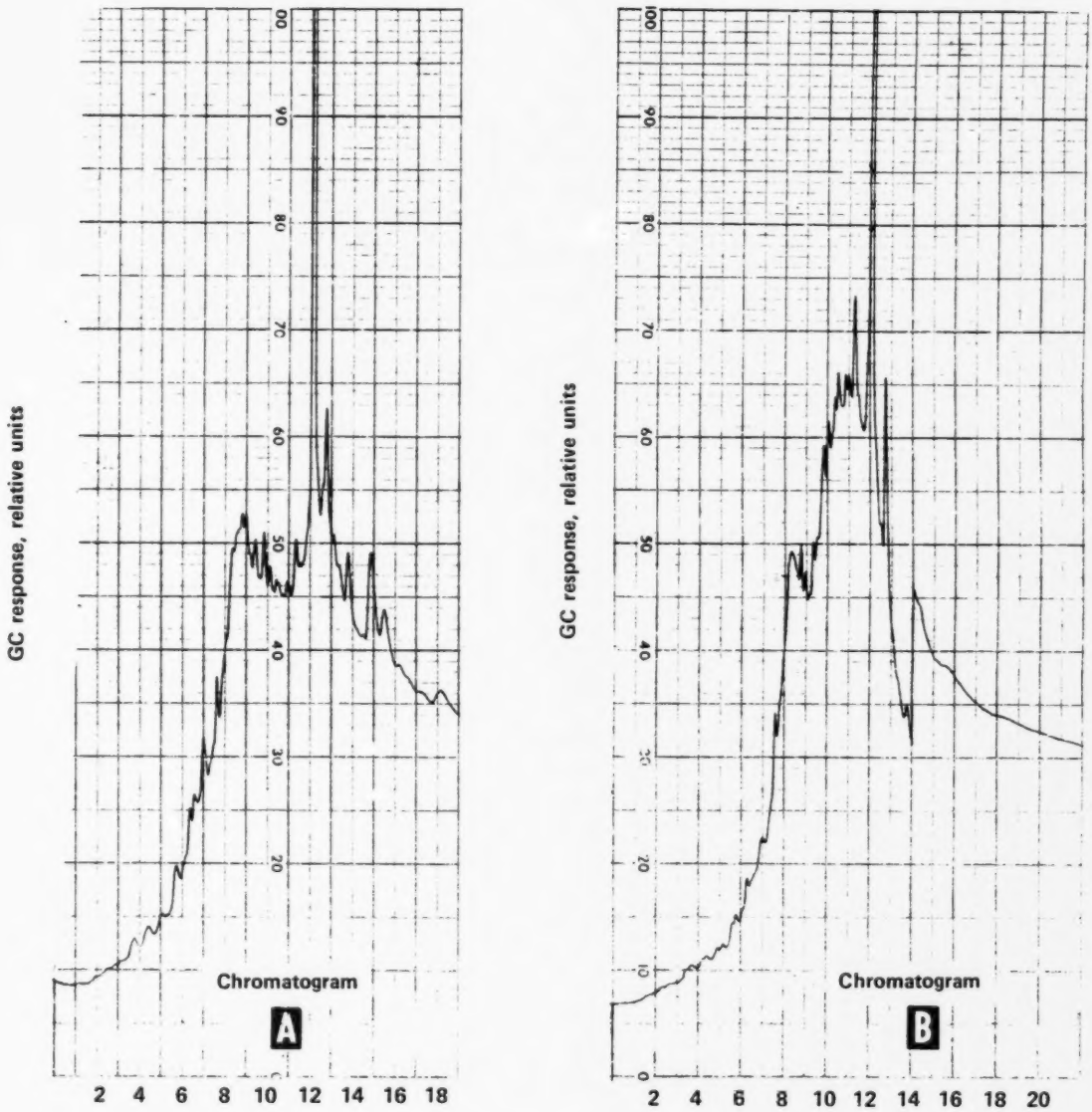

Figure 14. Flame ionization detector chromatograms of flue gas samples adsorbed on Gas-Chrom Q.